24. *Studies in the Polyene Series. Part XXI. Ethynylcarbinols from αβ-Unsaturated Ketones : their Anionotropic Rearrangements and other Reactions.*

By J. Cymerman, I. M. Heilbron, and E. R. H. Jones.

A careful study of the reaction conditions reveals that by using several mols. of sodium acetylide, made from sodamide in liquid ammonia solution, ethynylcarbinols from methyl vinyl ketone, ethylideneacetone, and mesityl oxide can be prepared in 40—55% yields. The carbinols all undergo anionotropic rearrangements on treatment with acids, although that derived from methyl vinyl ketone required the use of 10% sulphuric acid, a behaviour not unexpected, however, in view of the inability of vinylethynylcarbinol to rearrange with 25% acid. The structures of the isomerisation products are indicated by their absorption spectra and rigidly proved by complete hydrogenation to known saturated carbinols. The ethynylcarbinol from ethylideneacetone has been partly hydrogenated to the vinylcarbinol which rearranges to the secondary, rather than to the primary, dienol.

The procedure outlined above fails to give a reasonable yield of the ethynylcarbinol from *iso*phorone. Hexynylmagnesium bromide, however, yields the tertiary carbinol (XIV), which is exceptionally sensitive to acids. With 0·01% sulphuric acid the isomeric tertiary carbinol (XV) is formed, but the use of stronger acids leads to dehydration.

Both active hydrogen atoms in conjugated ethynylvinylcarbinols (*e.g.*, II), unlike those of their unconjugated isomers, react completely in the cold with methylmagnesium iodide in Zerewitinoff determinations (cf. Part VI).

Only two examples of the condensation of αβ-unsaturated ketones with acetylene can be found in the literature, and in both cases comparatively complex ketones were employed. The ethynylcarbinol from β-ionone was prepared by Gould and Thompson (*J. Amer. Chem. Soc.*, 1935, **57**, 340), using potassium *tert.*-amyloxide as condensing agent, and by Davies, Heilbron, Jones, and Lowe (J., 1935, 586), using sodamide. Clemo and Hoggarth (J., 1941, 476) condensed 5-keto-6 : 9-rubanene with acetylene, employing potassium *tert.*-amyloxide. With simple ketones, such as methyl vinyl ketone, which easily polymerise, the use of reagents of the above type is impracticable. It has already been shown, however (Jones and McCombie, J., 1942, 733), that condensations between αβ-unsaturated aldehydes and sodium acetylide can be carried out in liquid ammonia solution, and therefore the application of the method to αβ-unsaturated ketones has been studied in detail.

When equimolecular quantities of αβ-unsaturated ketones and sodium acetylide are mixed in liquid ammonia solutions, the ethynylcarbinols are formed only in low yields of the order of 15%. Numerous attempts were made to vary the time of reaction and also the temperature; some experiments carried out at room temperature under pressure, and also experiments employing an excess of the ketone, met with little success. The first promising indications were obtained when an excess of sodium acetylide was employed, and with the more reactive form of the latter reagent, prepared from sodamide instead of from sodium, in liquid ammonia solution (as described in Part XVIII) reasonable yields of the desired carbinols were obtained.

By this means, 4·5 mols. of sodium acetylide being employed, methyl vinyl ketone is converted in 40% yield into the tertiary *carbinol* (I; $R_1 = R_2 = H$), which gives an *α-naphthylurethane* on long standing, and, like the other carbinols of type (I) described below, contains two active hydrogen atoms and fails to show any absorption of appreciable intensity in the ultra-violet. With 6 mols. of sodium acetylide, ethylideneacetone

$$\text{(I.)}\quad CR_1R_2{:}CH\cdot CMe(OH)\cdot C{\vdots}CH \xrightarrow{\text{acid}} CR_1R_2(OH)\cdot CH{:}CMe\cdot C{\vdots}CH\quad\text{(II.)}$$

gives 3-*methylhex*-4-*en*-1-*yn*-3-*ol* (I; $R_1 = H$, $R_2 = Me$) in 40% yield, and from mesityl oxide on treatment with 3 mols. of sodium acetylide a 55% yield of 3 : 5-*dimethylhex*-4-*en*-1-*yn*-3-*ol* (I; $R_1 = R_2 = Me$) (*α-naphthylurethane*) can be obtained.* The structure of the latter carbinol was proved by hydrogenation to 3 : 5-dimethylhexan-3-ol (*phenylurethane*) which was compared with a specimen made by reaction between ethylmagnesium bromide and methyl *iso*butyl ketone.

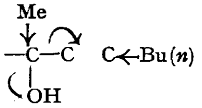
The facile rearrangement of the acetylenylcarbinols derived from αβ-unsaturated aldehydes, first described by Jones and McCombie (Part VIII; J., 1943, 261), has been considerably extended (Parts IX—XX). In Part XVI (Cymerman, Heilbron, and Jones, J., 1944, 144) the conversion of carbinols (*e.g.*, III), prepared by condensation of hexynylmagnesium bromide and αβ-unsaturated ketones, into the conjugated acetylenylvinylcarbinols (*e.g.*, IV) was reported, and it was pointed out that the rearrangements were more facile than

$$\text{(III.)}\quad CH_3\cdot[CH_2]_3\cdot C{\vdots}C\cdot C(OH)Me\cdot CH{:}CH_2 \xrightarrow{\text{acid}} CH_3\cdot[CH_2]_3\cdot C{\vdots}C\cdot CMe{:}CH\cdot CH_2\cdot OH\quad\text{(IV.)}$$

those of closely related secondary carbinols. It was suggested that the increased mobility of the anionotropic system was occasioned mainly by the inductive effect of the methyl group and a similar effect would be expected with the carbinols (I) described above.

It has already been reported (Jones and McCombie, *loc. cit.*) that vinylethynylcarbinol (V) fails to isomerise on treatment with 25% sulphuric acid. Its homologue (I; $R_1 = R_2 = H$), containing a tertiary hydroxyl group, is completely rearranged to (II; $R_1 = R_2 = H$) by shaking with 10% sulphuric acid for 42 hours, but with 5% acid for 18 hours isomerisation only occurs to the extent of about 25%, and with 1% acid for 24 hours the carbinol is unaffected. The marked effect of the additional methyl group is thus again apparent. On the other hand, the system present in the hexynylcarbinol (III) is clearly much more mobile than that in the

$$\text{(V.)}\quad CH_2{:}CH\cdot CH(OH)\cdot C{\vdots}CH$$



$$-\overset{\overset{Me}{\downarrow}}{C}-C\quad C\leftarrow Bu(n)$$

(VI.)

ethynylcarbinol (I; $R_1 = R_2 = H$), since (III) is quantitatively isomerised by shaking with 0·5% sulphuric acid for 4 hours. This fact draws attention to the significance of the *n*-butyl group which, owing to its electron-repelling tendency, decreases the electron-attracting properties of the acetylenic bond, as indicated diagrammatically in (VI). A similar effect can also be produced by semihydrogenation of the triple bond (Part XIX), resulting in a greater ease of rearrangement in the case of propenylvinylcarbinol (VII) as compared with propenylethynylcarbinol (VIII).

$$\text{(VII.)}\quad CH_3\cdot CH{:}CH\cdot CH(OH)\cdot CH{:}CH_2 \qquad\qquad CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}CH\quad\text{(VIII.)}$$

The rearranged *carbinol* (II; $R_1 = R_2 = H$) contains two active hydrogen atoms (Zerewitinoff) and, as would be expected of a primary alcohol, it rapidly forms an *α-naphthylurethane*. Its light-absorption properties (Table) are characteristic of those of the conjugated vinylacetylene chromophore, and its structure is finally proved by complete hydrogenation to 3-methylpentan-1-ol. When the carbinol (1; $R_1 = H$; $R_2 = Me$) is isomerised with 1% sulphuric acid it yields 4-*methylhex*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = H$, $R_2 = Me$), characterised as its

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
3-Methylpent-2-en-4-yn-1-ol (II; $R_1 = R_2 = H$)	2235	13,000
	2280	11,500
4-Methylhex-3-en-5-yn-2-ol (II; $R_1 = H$, $R_2 = Me$)	2230	13,000
	*2340	11,500
2 : 4-Dimethylhex-3-en-5-yn-2-ol (II; $R_1 = R_2 = Me$)	2240	12,500
	*2280	11,500
Hex-3-en-5-yn-2-ol [1]	2230	13;500
	*2300	9,500

* Inflexions. [1] Jones and McCombie (*loc. cit.*).

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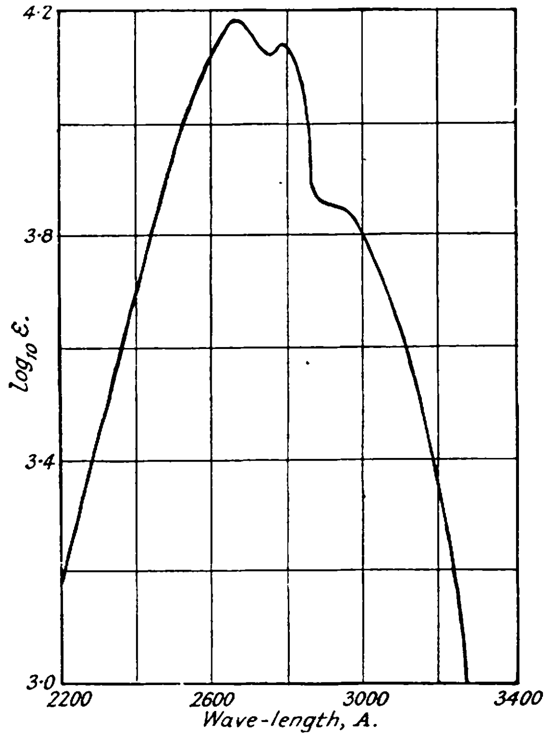
* Since this paper was written, Hennion and Lieb (*J. Amer. Chem. Soc.*, 1944, **66**, 1289) have described condensations of sodium acetylide in liquid ammonia with methyl vinyl ketone, ethylideneacetone, and mesityl oxide. Although the constants of the ethynylcarbinols so prepared are in complete agreement with those recorded in this paper, the yields quoted range from 21 to 27%.

phenylurethane, giving the expected light absorption (Table) and active hydrogen values, and hydrogenated to 4-methylhexan-2-ol (3 : 5-*dinitrobenzoate*). The carbinol (I; $R_1 = R_2 =$ Me) from mesityl oxide, when shaken with 0·5% sulphuric acid gives 2 : 4-*dimethylhex*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = R_2 =$ Me) (for light absorption, see Table).

As would be expected from the results described in Part XIX, partial hydrogenation of the acetylenic linkage in (I; $R_1 =$ H, $R_2 =$ Me) proceeds smoothly with a 0·3% palladium–calcium carbonate catalyst yielding 3-*methylhexa*-1 : 4-*dien*-3-*ol* (IX). It has already been shown (Part XIX) that these vinylcarbinols isomerise readily to the conjugated dienols, and in the case of (IX) two possibilities, (X) and (XI), are evident. Treatment of (IX) with 0·5% sulphuric acid gives a 50% yield of a homogeneous dienol which must be 4-*methylhexa*-3 : 5-*dien*-2-*ol* (X), since by complete hydrogenation it is converted into 4-methylhexan-2-ol. The dienol exhibits high-intensity absorption at 2290 A. (ε = 24,000) and, according to the generalisations of Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 72) concerning the effect of substituents on the location of the absorption maxima of conjugated diene systems, the maximum at 2290 A. is closer to that which would be expected for (X) ($\lambda_{max.}$ 2270 A.) than for (XI) ($\lambda_{max.}$ 2320 A.). The location is practically identical with that observed in Part XIX for a dienol (XII) structurally similar to (X). On reacting with maleic anhydride, (X) behaves in the manner characteristic (Part XIX) of conjugated dienols and yields the lactonic *acid* (XIII).

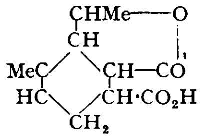
(IX.) $CH_3{\cdot}CH{:}CH{\cdot}\overset{*}{C}Me(OH){\cdot}CH{:}CH_2$
(X.) $CH_3{\cdot}CH(OH){\cdot}CH{:}CMe{\cdot}CH{:}CH_2$

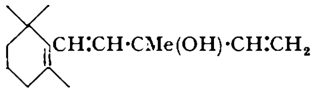
$CH_3{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$ (XI.)
$OH{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH_2$ (XII.)



The nature of the rearrangement product in this case is that expected by analogy with the behaviour of propenylvinylcarbinol (VII) towards acids, the secondary rather than the primary carbinol being obtained (Part XIX). The only effect produced by the additional methyl group (* in IX) is that of increasing the mobility of the tautomeric system, as has already been noted with the ethynyl- and hexynyl-carbinols derived from $\alpha\beta$-unsaturated ketones. Gould and Thompson (*loc. cit.*) have described the conversion of the vinylcarbinol (XIV) derived from β-ionone into the primary bromide, by treatment with phosphorus tribromide and pyridine. From the results described in this and preceding papers in this series, although it would be expected that the above vinylcarbinol would be very easily isomerised, the formation of the *primary* bromo-compound appears improbable. It is conceivable, however, that factors as yet unpredictable, especially steric influences due to the presence of the unsaturated ring system, may be involved. The failure of Thompson, Milas, and Rovno (*J. Amer. Chem. Soc.*, 1941, **63**, 752) to effect rearrangement of a carbinol which they formulate as (XV) is surprising, but the desired primary carbinol seems to us to be the less likely isomerisation product. The conditions employed for the attempted isomerisations were perhaps not ideal, no indications are given of the methods employed for detecting the expected product, and the absence of light-absorption data leaves some room for doubt as to the structure of the parent carbinol.

(XIII.)

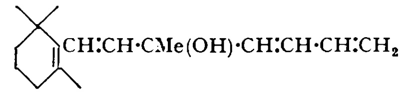


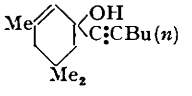


(XIV.)

An attempt has been made to extend some of the observations made above to cyclic $\alpha\beta$-unsaturated ketones. *iso*Phorone reacts only to a minor extent even with a large excess of sodium acetylide in liquid ammonia. With hexynylmagnesium bromide, however (as described in Part XVI), it reacts readily and, after allowance for recovered ketone, is converted into the tertiary *carbinol* (XVI) in 85% yield. This carbinol is very sensitive towards acids, and in the presence of 0·01% sulphuric acid it undergoes rearrangement to the carbinol (XVII)

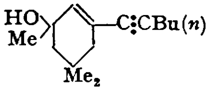
(XV.)

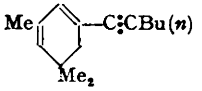


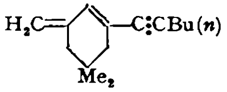


(XVI.)

which absorbs at 2280 A. (ε = 13,500), as might be expected. With more concentrated acids, rearrangement is followed by complete dehydration; *e.g.*, with 0·5% sulphuric acid a *hydrocarbon* is obtained which, on account of its light-absorption properties (Fig.), is considered to consist of a mixture of (XVIII) and (XIX), predominantly the latter. The maxima at 2660 and 2780 A. can be attributed to the form (XIX) containing the exocyclic methylene group, and the inflexion at 2915 A. to (XVIII) containing the fully cyclic diene chromophore, which by itself would be expected to absorb in the region of 2650 A. (cf. Booker, Evans, and Gillam, J., 1940, 1453). Ozonolysis of the hydrocarbon mixture gave formaldehyde, estimated as the dimedon derivative, in 50% yield, proving the presence in major proportion of (XIX).


(XVII.)


(XVIII.)


(XIX.)

In Part VI (J., 1942, 733) attention was directed to the behaviour of simple ethynylcarbinols during Zerewitinoff determinations of active hydrogen by means of methylmagnesium iodide, and it was noted that, whereas the hydroxyl group generally reacts completely in the cold, heating to 90° is necessary to complete the reaction with the acetylenic hydrogen atom. Many additional examples of this phenomenon have been encountered during the course of this work, but it has been observed that in the case of conjugated ethynylvinylcarbinols (such as II), replacement of the acetylenic hydrogen atom usually proceeds to completion in the cold. This implies that the hydrogen atom is more acid in character, *i.e.*, that the $\equiv$C–H bond becomes weaker. This can be visualised as being consequent upon the contribution of electrons from the triple bond to the resonance form of the conjugated vinylacetylene system. It has previously been noted that, unlike the alkylacetylenes, vinyl- and phenyl-acetylenes form potassium derivatives even with powdered potassium hydroxide in ethereal suspension, and also that replacement halogenation of the acetylenic hydrogen atom is more facile with these conjugated compounds.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

3-*Methylpent*-4-*en*-1-*yn*-3-*ol* (I; $R_1 = R_2 = H$).—To a solution of sodium acetylide, prepared from sodium (36 g.) in liquid ammonia (1 l.) by using the ferric nitrate catalyst of Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120) to catalyse the formation of sodamide, a solution of methyl vinyl ketone (24 g.) in dry ether (250 c.c.) was added during 1½ hours with stirring and cooling (acetone–solid carbon dioxide). The mixture was stirred and cooled for a further 1½ hours; ammonium chloride (100 g.) was then added, and the ammonia allowed to evaporate off overnight. The product was isolated by means of ether, and distillation through a column with a packed section (30 × 1·5 cm.) of single-turn glass helices gave 3-*methylpent*-4-*en*-1-*yn*-3-*ol* (12·5 g.) as a colourless pleasant-smelling liquid, b. p. 63·5—64·5°/100 mm., $n_D^{15^\circ}$ 1·4490 (Found: C, 75·1; H, 8·45. C_6H_8O requires C, 75·0; H, 8·4%). *Active hydrogen* (Zerewitinoff): At 20°/768 mm. the carbinol (57 mg.) rapidly evolved 14·2 c.c. of methane and a further 14·6 c.c. after being heated to 90°, equivalent to 1·0 and 2·05 active hydrogen atoms per mol. respectively. Neither this carbinol, nor those from ethylideneacetone or mesityl oxide, described below, showed light absorption of appreciable intensity in the ultra-violet. The α-*naphthylurethane*, formed after 5 months' standing at 20°, crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 110—111° (Found: N, 5·45. $C_{17}H_{15}O_2N$ requires N, 5·3%).

3-*Methylhex*-4-*en*-1-*yn*-3-*ol* (I; $R_1 = H$, $R_2 = Me$).—Prepared from ethylideneacetone (42 g.) and sodium (69 g.) by the method described above, the *carbinol* (21·5 g.) had b. p. 59°/23 mm., $n_D^{19^\circ}$ 1·4550 (Found: C, 76·45; H, 9·2. $C_7H_{10}O$ requires C, 76·3; H, 9·15%). *Active hydrogen*: At 22°/766 mm. the carbinol (55 mg.) rapidly evolved 12·7 c.c. of methane, and a further 11·6 c.c. after being heated to 90° (1·0 and 1·95 active hydrogen atoms per mol. respectively).

3 : 5-*Dimethylhex*-4-*en*-1-*yn*-3-*ol* (I; $R_1 = R_2 = Me$).—The method described above, using mesityl oxide (98 g.) and sodium (69 g.), gave the *carbinol* (68 g.), b. p. 92·5—93·5°/70 mm., 67—67·5°/22 mm., $n_D^{22^\circ}$ 1·4619, as a colourless pleasant-smelling liquid (Found: C, 77·55; H, 10·2. $C_8H_{12}O$ requires C, 77·4; H, 9·75%). *Active hydrogen*: At 23°/770 mm. the carbinol (60 mg.) evolved 12·5 c.c. of methane and a further 11·5 c.c. on heating to 90° (1·05 and 2·05 active hydrogen atoms per mol. respectively). The α-*naphthylurethane*, obtained after keeping an equimolar mixture of the reactants in a sealed tube at 20° for 3 months, crystallised from light petroleum (b. p. 60—80°) in rhombs, m. p. 129·5—130° (decomp.) (Found: N, 4·9. $C_{19}H_{19}O_2N$ requires N, 4·8%).

3 : 5-*Dimethylhexan*-3-*ol*.—Hydrogenation of 3 : 5-dimethylhex-4-en-1-yn-3-ol (5·4 g.) in ethyl acetate (20 c.c.), using platinic oxide (100 mg.) as catalyst, gave 3 : 5-dimethylhexan-3-ol (5·2 g.), b. p. 62—63°/22 mm., $n_D^{21^\circ}$ 1·4268. A synthetic specimen made from ethylmagnesium bromide and methyl *iso*butyl ketone had b. p. 60—60·5°/20 mm., $n_D^{21^\circ}$ 1·4265 (Meyr and Tuot, *Compt. rend.*, 1933, **196**, 1231, give b. p. 59°/15 mm., $n_D^{20^\circ}$ 1·4266). Identical *phenylurethanes* were obtained from either specimen of carbinol, after equimolar mixtures of carbinol and phenyl *iso*cyanate had been kept for 5 months. They separated from light petroleum (b. p. 40—60°) in needles, m. p. 62—63°, undepressed on admixture with each other (Found: N, 5·6. $C_{15}H_{23}O_2N$ requires N, 5·6%).

3-*Methylpent*-2-*en*-4-*yn*-1-*ol* (II; $R_1 = R_2 = H$).—3-Methylpent-4-en-1-yn-3-ol (4·4 g.) was shaken with sulphuric acid (80 c.c.; 10% w/v) for 42 hours at 20° in nitrogen. Ether extraction gave 3-*methylpent*-2-*en*-4-*yn*-1-*ol* (3·5 g.), b. p. 85—87°/50 mm., 66—66·5°/30 mm., $n_D^{16^\circ}$ 1·4850, as a colourless oil which rapidly became yellow on keeping (Found: C, 75·3; H, 8·4. C_6H_8O requires C, 75·0; H, 8·4%). *Active hydrogen*: At 20°/767 mm. the carbinol (32 mg.) rapidly evolved 7·9 c.c. of methane, and a further 7·8 c.c. after prolonged shaking (1·0 and 2·0 active hydrogen atoms per mol., respectively). The α-*naphthylurethane*, formed from the mixed reactants in 1 hour at 20°, crystallised in needles, m. p. 119°, from light petroleum (b. p. 60—80°) (Found: N, 5·3. $C_{17}H_{15}O_2N$ requires N, 5·3%).

3-*Methylpentan*-1-*ol*.—A solution of 3-methylpent-2-en-4-yn-1-ol (2 g.) in methyl acetate (20 c.c.) was shaken with hydrogen in the presence of platinic oxide (100 mg.) until absorption ceased. Removal of catalyst and solvent gave 3-methylpentan-1-ol (1·6 g.), b. p. 152—153°/763 mm., $n_D^{21^\circ}$ 1·4200 (Olivier, *Rec. Trav. chim.*, 1936, **55**, 1027, gives b. p. 152—153°, and Levene and Rothen, *J. Biol. Chem.*, 1936, **116**, 209, give $n_D^{25^\circ}$ 1·4178). The 3 : 5-dinitrobenzoate separated from light petroleum (b. p. 40—60°) as colourless needles, m. p. 37—38° (Sutter, *Helv. Chim. Acta*, 1938, **21**, 1266, gives m. p. 38°).

4-*Methylhex*-3-*en*-5-*yn*-2-*ol* (II; R_1 = H, R_2 = Me).—A mixture of 3-methylhex-4-en-1-yn-3-ol (7 g.) and sulphuric acid (500 c.c.; 1% w/v) was shaken for 14 hours at 20° giving 4-*methylhex*-3-*en*-5-*yn*-2-*ol* (6·1 g.), b. p. 71·5—72°/20 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4740, as a colourless liquid rapidly turning yellow on keeping (Found : C, 76·2; H, 9·1. $C_7H_{10}O$ requires C, 76·3; H, 9·15%). *Active hydrogen :* At 23°/764 mm. the carbinol (65 mg.) rapidly gave 14·3 c.c. of methane and a further 14·7 c.c. after heating to 90° (1·0 and 2·05 active hydrogen atoms per mol., respectively). The *phenylurethane* crystallised from methyl alcohol in plates, m. p. 94—95° (Found : N, 6·3. $C_{14}H_{15}O_2N$ requires N, 6·1%).

4-*Methylhexan*-2-*ol* and 4-*Methylhexan*-2-*one*.—A solution of 4-methylhex-3-en-5-yn-2-ol (5·5 g.) in methyl acetate (30 c.c.) was hydrogenated with platinic oxide (100 mg.) as catalyst and gave 4-methylhexan-2-ol (5·3 g.), b. p. 148—150°/767 mm., 80—82°/50 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4302 (Levene and Marker, *J. Biol. Chem.*, 1931, **91**, 761, give b. p. 146—147°/760 mm.). The 3 : 5-*dinitrobenzoate* separated from methyl alcohol in needles, m. p. 51° (Found : N, 9·05. $C_{14}H_{18}O_6N_2$ requires N, 9·05%). Oxidation of the alcohol (2·35 g.) with chromic acid in sulphuric acid gave the ketone (1·9 g.), b. p. 62—65°/50 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4118, which probably contained a little unchanged carbinol. The semicarbazone crystallised from aqueous methyl alcohol in plates, m. p. 129° (Chavanne, *Bull. Soc. chim. Belg.*, 1927, **36**, 206, gives m. p. 129°). The ketone regenerated from the pure semicarbazone by boiling with hydrochloric acid (15%) for 1 hour had b. p. 140—142°, $n_{\mathrm{D}}^{20^\circ}$ 1·4092 (Johnson and Hager, *Org. Synth.*, Coll. Vol. I, 343, give b. p. 139—142°, and Cope, Hofmann, and Hardy, *J. Amer. Chem. Soc.*, 1941, **63**, 1852, give $n_{\mathrm{D}}^{25^\circ}$ 1·4057).

2 : 4-*Dimethylhex*-3-*en*-5-*yn*-2-*ol* (II; $R_1 = R_2$ = Me).—3 : 5-Dimethylhex-4-en-1-yn-3-ol (20 g.) was isomerised by shaking with sulphuric acid (2 l.; 0·5% w/v) at 20° for 6 hours to 2 : 4-*dimethylhex*-3-*en*-5-*yn*-2-*ol* (15 g.), a pleasant-smelling liquid, b. p. 65—66°/20 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4711 (Found : C, 77·2; H, 9·85. $C_8H_{12}O$ requires C, 77·4; H, 9·75%). *Active hydrogen :* At 24°/769 mm. the carbinol (45 mg.) rapidly evolved 9·9 c.c. of methane and a further 8·2 c.c. on heating to 50° (equivalent to 1·1 and 2·0 active hydrogen atoms per mol. respectively).

3-*Methylhexa*-1 : 4-*dien*-3-*ol* (IX).—A solution of 3-methylhex-4-en-1-yn-3-ol (11 g.) in methyl acetate (30 c.c.) was shaken with hydrogen in the presence of palladium–calcium carbonate (1 g.; 0·3%) until about 2·35 l. of gas at 17°/767 mm. had been absorbed. The catalyst was filtered off and the solvent removed through a column, and distillation of the residue gave 3-*methylhexa*-1 : 4-*dien*-3-*ol* (10·7 g.), b. p. 41·5—42·5°/15 mm.; 56—58°/28 mm., $n_{\mathrm{D}}^{23^\circ}$ 1·4485 (Found : C, 74·95; H, 10·85. $C_7H_{12}O$ requires C, 74·95; H, 10·8%). *Active hydrogen* (Zerewitinoff) : The carbinol (49 mg.) evolved 10·6 c.c. of methane at 20°/769 mm. (1·0 active hydrogen atom per mol.), and showed no light absorption of appreciable intensity in the ultra-violet.

4-*Methylhexa*-3 : 5-*dien*-2-*ol* * (X) (with J. T. McCombie).—A mixture of the preceding carbinol (6 g.) and sulphuric acid (400 c.c.; 0·5% w/v) together with a trace of quinol was shaken for 25 minutes at 20° under nitrogen. Isolation with ether gave 4-*methylhexa*-3 : 5-*dien*-2-*ol* (3 g.), b. p. 73—75°/14 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4878, together with much higher-b. p., resinous material (Found : C, 75·05; H, 11·15. $C_7H_{12}O$ requires C, 74·95; H, 10·8%). *Active hydrogen* (Zerewitinoff) : The carbinol (35 mg.) evolved 7·5 c.c. of methane at 20°/768 mm. (1·0 active hydrogen atom per mol.).

γ-*Lactone of* 4-*Methyl*-3-α-*hydroxyethyl*-Δ⁴-cyclo*hexene*-1 : 2-*dicarboxylic Acid* (XIII).—An equimolecular quantity of the preceding carbinol was added to maleic anhydride in dry benzene whereupon the anhydride completely dissolved and the temperature rose to 60—70°. The crystals which separated on standing and after cooling were recrystallised from benzene or water, giving the lactonic *acid* as rectangular plates, m. p. 193—194° (Found : C, 62·9; H, 7·0. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·7%).

4-*Methylhexan*-2-*ol*.—A solution of 4-methylhexa-3 : 5-dien-2-ol (4 g.) in methyl acetate (15 c.c.) was shaken with hydrogen in the presence of platinic oxide (0·1 g.) until absorption ceased. The catalyst was filtered off and the solvent removed through a column, leaving a residue of 4-methylhexan-2-ol (3·8 g.), b. p. 81—82°/50 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4298 (cf. above). The 3 : 5-dinitrobenzoate crystallised from alcohol as needles, m. p. 51°, undepressed on admixiture with an authentic specimen.

1-(1′-*Hydroxy*-3′ : 5′ : 5′-*trimethyl*-Δ²-cyclo*hexenyl*)*hex*-1-*yne* (XVI).—To an ice-cold solution of hexynylmagnesium bromide (Cymerman, Heilbron, and Jones, *loc. cit.*), prepared from 1-hexyne (12·5 g.) and ethylmagnesium bromide (from 3 g. of magnesium), a solution of *iso*phorone (17·2 g.; b. p. 99°/21 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4785) in ether (200 c.c.) was added with stirring during 1½ hours. After a further 18 hours' stirring at 20° the Grignard complex was decomposed with ammonium chloride solution, and isolation of the product in the usual manner followed by distillation gave a forerun of *iso*phorone (10·2 g.) and the *carbinol* (10·1 g.), as a colourless viscous oil with a faint odour of eucalyptus; b. p. 107·5—108·5°/10^{-2} mm., 58° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4900 (Found: C, 81·7; H, 10·7. $C_{15}H_{24}O$ requires C, 81·75; H, 11·0%). *Active hydrogen* (Zerewitinoff) : The carbinol (116 mg.) evolved 12·6 c.c. of methane at 20°/763 mm. (1·0 active hydrogen atom per mol.). It showed no appreciable light absorption in the ultra-violet.

1-(3′-*Hydroxy*-3′ : 5′ : 5′-*trimethyl*-Δ¹′-cyclo*hexenyl*)*hex*-1-*yne* (XVII).—The preceding carbinol (1·2 g.) was treated with sulphuric acid (1000 c.c.; 0·01% w/v) containing acetone (300 c.c.) for 30 minutes at 20° under nitrogen. Isolation with ether afforded the rearranged *carbinol* (XVII) (1 g.), which has a faint camphoraceous odour, b. p. 54° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5019 (Found: C, 81·45; H, 11·4. $C_{15}H_{24}O$ requires C, 81·75; H, 11·0%). *Active hydrogen* (Zerewitinoff) : The carbinol (82 mg.) evolved 8·9 c.c. of methane at 19°/769 mm. (1·0 active hydrogen atom per mol.). *Light absorption* : Maximum, 2280 A.; ε = 13,500.

Simultaneous Rearrangement and Dehydration of (XVI).—The carbinol (5 g.) was treated with sulphuric acid (600 c.c.; 0·5% w/v) containing acetone (100 c.c.) for 16 hours at 20°. Isolation in the usual manner gave a product, $n_{\mathrm{D}}^{19^\circ}$ 1·5160. *Light absorption :* Maximum, 2645 A.; ε = 11,500. Inflexion, 2780 A.; ε = 11,000. On distillation this gave a *hydrocarbon* (3·95 g.), b. p. 110—110·5°/5 mm., 42° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5150 (Found: C, 89·15; H, 10·9. $C_{15}H_{22}$ requires C, 89·05; H, 10·95%). *Light absorption :* Maxima, 2660 and 2780 A.; ε = 15,000 and 14,000, respectively. Inflexion, 2915 A., ε = 7,000.

Ozonolysis of Hydrocarbon.—A solution of the hydrocarbon (1 g.) in acetic acid (25 c.c.) was treated with a stream of ozonised oxygen at 20° for 2 hours, the issuing gases being passed into water. This solution and the reaction mixture were combined and steam-distilled after the addition of zinc dust (1 g.). The distillate, treated with an excess of dimedon according to Jonescu (*Bull. Soc. chim.*, 1930, **47**, 1408), gave 0·70 g. of the dimedon derivative (m. p. and mixed m. p. 188°), corresponding to a 50% yield.

Imperial College of Science and Technology, London, S.W. 7. [*Received, October* 19*th*, 1944.]

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* Patent application pending.